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**EFFECTS OF SOLVATION ON ONE- AND TWO-PHOTON
SPECTRA OF COUMARIN DERIVATIVES: A TIME-
DEPENDENT DENSITY FUNCTIONAL THEORY STUDY
(POSTPRINT)**

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Effects of solvation on one- and two-photon spectra of coumarin derivatives: A time-dependent density functional theory study

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We report one- and two-photon absorption excitation energies and cross sections for a series of 7-aminocoumarins using time-dependent density functional theory with various basis sets and functionals, including exchange-correlation functionals using the Coulomb-attenuating method, to evaluate their performance in the gas phase and in solvents. Except for the results of one functional, the computed one-photon excitation energies and transition dipole moments are in good agreement with experiment. The range of errors obtained from various functionals is discussed in detail. The relationship of donor and acceptor groups with the one- and two-photon resonances and intensities is also discussed. © 2007 American Institute of Physics. [DOI: [10.1063/1.2464110](https://doi.org/10.1063/1.2464110)]

I. INTRODUCTION

Coumarin derivatives that are formed by various substitutions of amino groups at the 7-position are widely used as probes in ultrafast solvation studies, as laser dyes,^{1,2} and as nonlinear optical chromophores^{3–5} in optoelectronic devices. Thus, pertinent optical properties for these applications have been extensively reported in the literature. Electronic one-photon absorption (OPA) spectra of coumarins, in particular, have been characterized in high temperature vapors,^{6,7} in a supersonic jet expansion,^{6–8} and in a variety of polar and nonpolar solvents.^{9–15} Experimental studies have revealed the polar nature of the first excited state that has been characterized as an intramolecular charge-transfer (ICT) state, implying a larger dipole moment than in the ground state. The large difference in dipole moment between the ground and excited states ($\Delta\mu_{ge}$) provides a viable mechanism for the intense two-photon absorption^{16–19} (TPA) and other nonlinear processes^{3,4} that have been observed and quantified for a number of coumarin derivatives.

Theoretically, OPA properties of coumarins in the gas phase have been reported in semiempirical studies using AM1,²⁰ PM3,^{21,22} and MNDO²³ methods. Recently, Cave *et al.*²⁴ reported a detailed theoretical study of coumarin 120 (C120) and C151 using a wide range of electronic structure methods to evaluate various ground and excited state properties. They found that using time-dependent density functional theory^{25–28} (TDDFT) with hybrid functionals gives excellent agreement with S_0 - S_1 experimental OPA excitation energies. In another survey²⁹ involving C102, C152, C153, and C343, excellent agreement with experiment was also reported for TDDFT excitation energies. Optical properties of C120,²⁴ C151,^{24,30–32} 152A (C35, C481),^{30,31} and C153 (Refs. 30 and 31) have been studied using TDDFT with continuum,²⁴ and explicit^{30–32} solvent models. Recently, In-

grosso *et al.* reported³³ a solvation study of C153 in supercritical fluoroform using TDDFT with Becke's three-parameter^{34–36} (B3LYP) hybrid functional. More recently, TDDFT calculations using the conventional model^{37,38} and the state specific³⁹ polarizable continuum model (PCM) have been carried out for C153. The successful applications of TDDFT with hybrid functionals for coumarins are consistent with our previous studies⁴⁰ on the prediction of excitation energies involving charge-transfer excited states. However, we found that the B3LYP functional^{34–36} and the hybrid functional of Perdew, Burke, and Erzerhof^{41,42} (PBE0) underestimate the experimental excitation energies of a number of ICT chromophores. Both functionals were found to overestimate the oscillator strengths for the first ICT excited states. The failures to provide a good description for ICT excited states have been attributed to the incorrect long-range behavior of the exchange potential.^{43,44} Thus, a detailed comparison between computed and experimental OPA and TPA excitation energies and intensities for a series of coumarins was carried out to assess the accuracy that can be achieved with the B3LYP, PBE0, and the new long-range-corrected functional of Handy and co-workers.^{43,44} Previous TDDFT studies on coumarins focused on the OPA excitation energy but not on intensity, and TPA spectra were not considered.

The aim of the present work is to investigate both the OPA and TPA spectra for a series of coumarin derivatives with different degrees of ICT character (Figs. 1 and 2) in the gas phase and in solvents. In 7-aminocoumarins, the amine and carbonyl moieties are expected to act as electron donor and acceptor, respectively. Thus, the 4-methyl coumarin derivatives (Fig. 1) with an increasing degree of alkylation measure the effects of different donor groups on the OPA and TPA spectra. The effects of the acceptor are also gauged by 4-trifluoromethyl coumarin derivatives (Fig. 2).

II. COMPUTATIONAL METHODS

The computation of excitation energies and cross sections was preceded by the determination of equilibrium ge-

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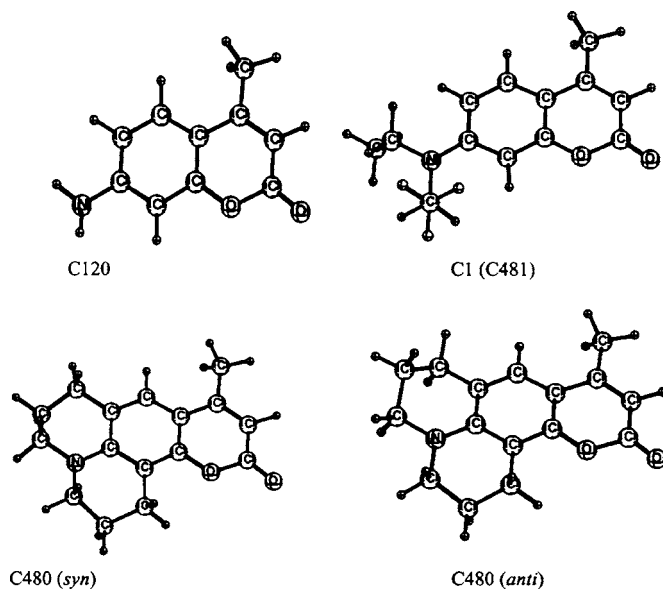


FIG. 1. Structure of coumarin 120, 1, 480 (102).

ometries, and then single point excited state calculations were carried out to obtain the vertical excitation energies, transition dipoles, and oscillator strengths. All structures have been predicted using the Kohn-Sham⁴⁵ density functional theory with the 6-311G(*d,p*) (Ref. 46) basis set and the B3LYP hybrid functional.^{34–36} These structures were verified to be minima on the potential energy surface with

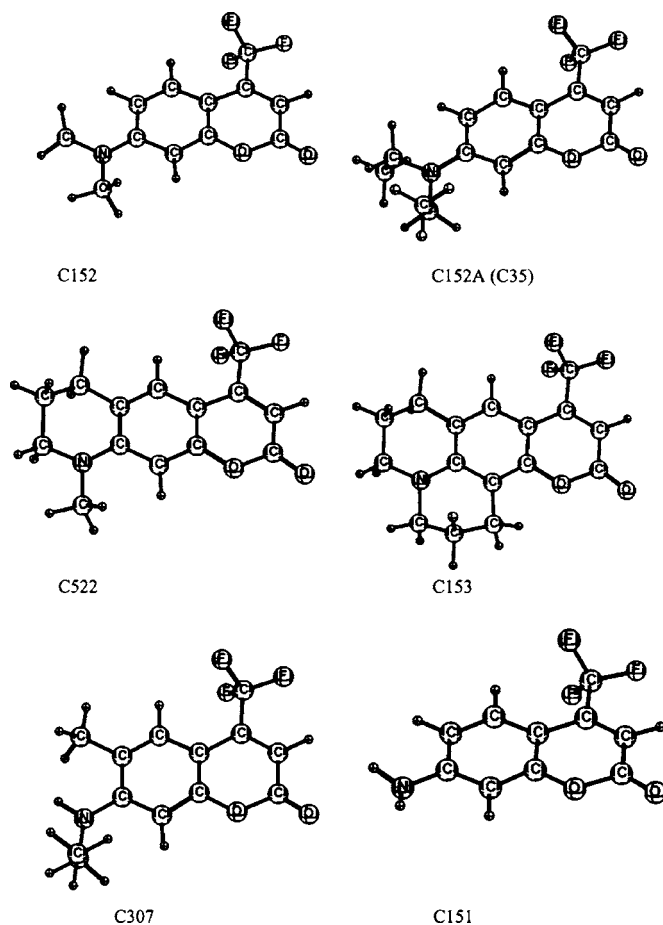


FIG. 2. Structure of coumarin 152, 152A, 522, 153, 307, and 151.

harmonic frequency calculations using the GAUSSIAN 03 program.⁴⁷ TDDFT calculations were carried out using the 6-311G(*d,p*), 6-311++G(*d,p*), and aug-cc-pVTZ (for selected cases) basis sets with the B3LYP, PBE0, and the new hybrid functional of Yanai *et al.*,⁴³ as implemented in the DALTON program.⁴⁸ This hybrid functional, called CAMB3LYP, combines properties of B3LYP and the long-range correction for the exchange potential by an Ewald split of the r_{12}^{-1} operator into⁴³

$$r_{12}^{-1} = \frac{1 - [\alpha + \beta \operatorname{erf}(\mu r_{12})]}{r_{12}} + \frac{\alpha + \beta \operatorname{erf}(\mu r_{12})}{r_{12}}, \quad (1)$$

where μ , α , and β are empirical parameters. Yanai *et al.* found that the CAMB3LYP functional yields the smallest mean absolute error (MAE=2.53 kcal/mol) with $\mu=0.33$, $\alpha=0.19$, and $\beta=0.46$ ($\alpha+\beta=0.65$) in atomization energies for the G2 set. This is slightly better than the corresponding MAE of 2.68 kcal/mol for B3LYP, which is nearly equivalent to setting $\alpha=0.2$ and $\beta=0.0$ in CAMB3LYP.⁴⁴ However, the ICT excitation energies for a model dipeptide are greatly improved, when compared to the CASPT2 results. In addition, we tested a modified CAMB3LYP (*m*CAMB3LYP) functional with a two-parameter Ewald split of the r_{12}^{-1} operator as

$$r_{12}^{-1} = \frac{1 - [\alpha + \alpha \operatorname{erf}(\mu r_{12})]}{r_{12}} + \frac{\alpha + \alpha \operatorname{erf}(\mu r_{12})}{r_{12}}, \quad (2)$$

where μ and α are kept unchanged.

To account for the solvent effects, TDDFT calculations were carried out with the nonequilibrium PCM (Refs. 37 and 38) and the self-consistent reaction field (SCRF) model of Mikkelsen *et al.*,⁴⁹ which uses a spherical solute cavity (SCRF-S). The PCM solute cavities were carried out using the united atom topological model and empirical solvent radii, as implemented in the GAUSSIAN 03 program.⁴⁷ The radii (a_0) for the SCRF-S were obtained using the largest interatomic distances of the solutes with added adjustments for van der Waals interactions. The SCRF-S calculations were carried out using the DALTON program.⁴⁸

The TPA cross sections can be obtained by relating the absorption rate^{40,50} to the TPA transition probability, which was first derived by Goppert-Mayer (GM) using second order perturbation theory.⁵¹ The two-photon absorptivity δ_{f0} between the ground state (0) and the final state *f* is written as^{40,52,53}

$$\delta_{f0}(E_1, E_2) = \frac{8\pi^4}{(ch)^2} E_1 E_2 \sum_f g_{f0}(E_1, E_2) |S_{f0}(E_1, E_2)|^2, \quad (3)$$

where *c* is the speed of light, *h* is Planck's constant, E_λ the photon energies, and $g_{f0}(E_1, E_2)$ is the normalized line shape function for the ground to *f* transition, which can be represented by a Gaussian or a Lorentzian. The two-photon matrix elements $S_{f0}(E_1, E_2)$ were obtained from single (SRQR) or double (DRQR) residue of the quadratic response function of the electric dipole operator⁵⁴ within the framework of TDDFT.⁵⁵ TPA cross section calculations with DRQR are carried out using the sum-over-state (SOS) method. These calculations were carried out with the DALTON program.⁴⁸

The excited state dipoles are computed using the DRQR method or the finite field method with an applied field of ± 0.0001 a.u.

III. RESULTS AND DISCUSSION

The OPA results are briefly summarized in Table I while all the results are organized in an expanded version of the table in the EPAPS (Ref. 68) Supporting Information Section. The TPA results are tabulated in Tables II–IV. Table I lists the computed excitation energies, transition dipole moments (μ_{ge}), and oscillator strengths (f) along with available experimental values. The experimental energies are obtained from the maxima of the absorption band, which were integrated (using Gaussian line shapes) to obtain the transition moments and oscillator strengths in cases where the absolute intensities were available. We note that the gas-phase B3LYP excitation energies for C120 and C151 and the corresponding PBE0 values for C152 and C153 are identical to those reported by Castner and co-workers.^{24,29} Table I also lists the OPA spectral properties in ethanol/methanol and cyclohexane. These solvents are chosen due to their widespread use as representatives for polar and nonpolar solvents for coumarins. We begin with the OPA spectra, and then discuss the TPA results, starting with the gas-phase spectra, the influence of basis sets, theoretical methods, and the effects of solvents and alkylation. Analysis of the basis set effect is limited to a few systems, which are found to be small. Thus, the results of the 6-311G(*d,p*) basis set are used for discussion throughout, unless noted otherwise.

A. One-photon absorption

We first compare the gas-phase results that are available for C152, C152A, C522, and C153 (Table I). For these coumarin derivatives, TDDFT excited state calculations are carried out at the B3LYP/6-311G(*d,p*) geometry using both the 6-311G(*d,p*) and 6-311++G(*d,p*) basis sets to gauge the effects of diffuse functions. For CAMB3LYP (using the recommended $\alpha=0.19$ and $\beta=0.46$ parameters) and the two widely used B3LYP and PBE0 functionals, the TDDFT excitation energies are slightly affected by the basis set. The augmentation of diffuse functions on hydrogen and heavy atoms lowers the excitation energies by about 0.1 eV for the S_0 - S_1 ICT energies, as predicted by B3LYP and PBE0. However, the corresponding changes are found to be quite small (0.02 eV) for the CAMB3LYP functional. Overall, the ICT experimental excitation energies are well reproduced with the 6-311G(*d,p*) basis set, which yields the MAEs of 0.03 and 0.08 eV for PBE0 and B3LYP, respectively. The corresponding MAEs of 0.16 and 0.05 eV are found for the 6-311++G(*d,p*) basis set, which has negligible differences in S_0 - S_1 excitation energies from the larger aug-cc-pVTZ basis set (see Table I). Note that B3LYP consistently underestimates the experimental excitation energies. The predicted CAMB3LYP/6-311G(*d,p*) ICT excitation energies yield a MAE of 0.32 eV. This is much larger than the corresponding MAE obtained with the PBE0 and B3LYP functionals. As illustrated for C152, the large deviations between B3LYP and CAMB3LYP can be attributed to the value of β [see Table IS

in the EPAPS (Ref. 68) Supporting Information Section], since $\beta=0$ for B3LYP ($\alpha=0.19$ nearly the same as in B3LYP). Thus, the α and β parameters must be reexamined for both the ground (e.g., the G2 set) and excited states. However, the effects of β on the ground state energetics are found to be small. The MAE of atomization in the G2 set for $\beta=0$ and $\beta=0.46$ changes from 2.68 to 2.53 kcal/mol, respectively.⁴³ Thus, the corresponding error for $\beta=\alpha=0.19$ [Eq. (2)] is likely within this range. The small compromise in the ground state energetics results in a significant improvement in the predicted S_0 - S_1 ICT energies, which have MAEs of 0.10 and 0.06 eV (without C153 due to convergence problem) for the 6-311G(*d,p*) and 6-311++G(*d,p*) basis sets, respectively. It is worth noting that excitation energies computed with the nonhybrid BLYP functional and Tamm-Dancoff approximation are computationally more economical but do not offer comparable accuracy delivered by TDDFT with the hybrid B3LYP, PBE0, or *m*CAMB3LYP functional. The predicted^{30,31} gas-phase S_0 - S_1 energies of 2.99 and 2.90 eV for C152A (C35) and C153, respectively, are significantly lower than the corresponding experimental values⁶ of 3.56 and 3.37 eV. For C151, the BLYP and SAOP gas-phase excitation energies of 3.32 (Refs. 30 and 31) and 3.24 eV,³² respectively, were reported. These predicted values are much lower than the experimental value of 3.70 eV in *n*-hexane.¹²

We now discuss the trends observed with the predicted results in the gas phase, which do not appear to be dependent upon the choice of basis and functionals. For example, the B3LYP and PBE0 (0.17 eV) S_0 - S_1 shifts for C152-C153 are identical for the 6-311G** and 6-311++G** basis sets. The predicted value of 0.17 eV is in good agreement with corresponding experimental value of 0.22 eV. All four functionals predict the S_0 - S_1 energy to shift to the red with an increasing degree of alkylation, C120 < C1 < C480. A trifluorine substitution at the 4-methyl group gives pronounced redshifts that increase in magnitude with a higher degree of alkylation (C151 < C307 < C152 < C152A < C522 < C153), in agreement with the experimental data⁶ for the latter four coumarins. We should note that the absorption maxima of C152 and C152A listed in Table I of Ref. 6 must be interchanged for them to be consistent with their corresponding absorption spectra given in Fig. 3 of their paper.

The continuum solvation models do not treat specific solvent-solute interactions such H bonding, which is important in water^{8,24} and methanol⁵⁶ but not in a cyclohexane solution. For the 6-311G(*d,p*) basis set, the SCRF-S model of cyclohexane overestimates the experimental S_0 - S_1 energies by 0.05, 0.22, and 0.42 eV for the B3LYP, *m*CAMB3LYP, and CAMBLYP, respectively. Using the same basis set, the MAEs for PCM with PBE0 and B3LYP are 0.03 and 0.11 eV, respectively. These excitation energies do not appear to be strongly affected by the addition of diffuse functions, which are found to lower the energies by 0.05–0.07 eV for C120 (see Table I). Thus, the 6-311G(*d,p*) basis set seems adequate for predicting S_0 - S_1 energies. Note that the errors for B3LYP are slightly improved compared to those obtained in the gas phase due to the effects of compensation in excitation energy by the SCRF-S method and the

TABLE I. 6-311G(*d,p*) excitation energy (*E*, eV), oscillator strength (*f*), and transition dipole moment (μ_{01} , D) for coumarin derivatives compared with experiment. The values in parentheses and brackets are computed with the 6-311++G(*d,p*) and the aug-cc-pVTZ basis sets, respectively.

System/method	$E(S_1)$	Theor. <i>f</i>	μ_{01}	Expt. Energy (μ_{01}) [<i>f</i>]	Solvent
C120					
CAMB3LYP	4.29 (4.24)	0.373 (0.368)	4.79 (4.79)		
PBE0	4.09 (4.04) [4.03]	0.348 (0.363) [0.355]	4.74 (4.87) [4.82]		
B3LYP	4.00 (3.94) [3.93]	0.329 (0.344) [0.338]	4.66 (4.80) [4.76]		
					EtOH
SCRF-S-CAMB3LYP ^a	4.07 (4.00)	0.479 (0.497)	5.57 (5.72)		
SCRF-S- <i>m</i> CAMB3LYP ^a	3.90 (3.83)	0.433 (0.451)	5.41 (5.57)		
PCM-PBE0	3.81 (3.74)	0.456 (0.477)	5.61 (5.80)		
SCRF-S-B3LYP ^a	3.76 (3.69)	0.390 (0.406)	5.23 (5.39)		
PCM-B3LYP	3.71 (3.64)	0.424 (0.445)	5.49 (5.68)	3.51 ^b (5.54) [0.318] ^{c,d}	
					Water
SCRF-S-CAMB3LYP ^c	(3.99)	(0.495)	(5.72)		
SCRF-S- <i>m</i> CAMB3LYP ^c	(3.81)	(0.447)	(5.56)		
SCRF-S-B3LYP ^c	(3.68)	(0.401)	(5.36)		
PCM-B3LYP	3.70 (3.63)	0.418 (0.439)	5.46 (5.65)	3.65 (4.85) [0.325] ^f	
					Cyclohexane
SCRF-S-CAMB3LYP ^g	4.19 (4.13)	0.467 (0.477)	5.42 (5.51)		
SCRF-S- <i>m</i> CAMB3LYP ^g	4.02 (3.97)	0.434 (0.446)	5.33 (5.44)		
SCRF-S-B3LYP ^g	3.89 (3.84)	0.401 (0.415)	5.22 (5.33)		
PCM-PBE0	3.93 (3.87)	0.472 (0.495)	5.63 (5.81)		
PCM-B3LYP	3.84 (3.77)	0.443 (0.468)	5.52 (5.72)	3.76 ^b	
C1					
B3LYP	3.72 (3.66) [3.65]	0.401 (0.409) [0.405]	5.33 (5.43) [5.41]		
PCM-B3LYP	3.47	0.490	6.10	3.32 ^b (5.63) [0.399] ^{d,h}	EtOH
PCM-B3LYP	3.57	0.510	6.13	3.54 ^f	Cyclohexane
C480					
B3LYP (<i>syn</i>)	3.60	0.347	5.04		
PCM-B3LYP (<i>anti</i>)	3.33	0.447	5.95		MeOH
PCM-B3LYP (<i>syn</i>)	3.34	0.433	5.85	3.19 (5.84) [0.412] ^{d,i}	MeOH
PCM-B3LYP	3.45	0.455	5.89	3.43 ^j	Cyclohexane
C151					
B3LYP	3.73 (3.66) [3.67]	0.312 (0.320) [0.317]	4.70 (4.80) [4.77]		
TDA-BLYP ^k	3.32				
SAOP/TZP ^l	3.24				
PCM-B3LYP	3.38	0.393	5.54	3.24 (4.97) [0.304] ^c	EtOH
MD-QMMM-SAP/TZP ^l	3.07			3.70 ^m	<i>n</i> -hexane
PCM-B3LYP	3.53	0.411	5.54	3.56 ⁿ	Cyclohexane
C307					
B3LYP	3.55	0.352	5.12		
PCM-B3LYP	3.27	0.431	5.89	3.15 (5.52) [0.364] ^o	MeOH
PCM-B3LYP	3.38	0.451	5.93	3.37 ^j	Cyclohexane
C152					
B3LYP	3.48 (3.40)	0.352 (0.348)	5.17 (5.20)	3.59 ^p	
PCM-B3LYP	3.20	0.427	5.93	3.13 ^f (5.31) [0.334] ^q	EtOH
C152A (C35)					
B3LYP	3.44 (3.35)	0.375 (0.372)	5.37 (5.41)	3.56 ^p	
TDA-BLYP ^k	2.99				
PCM-B3LYP	3.16	0.457	6.18	3.10 ^j (5.88) [0.408] ^{d,m}	EtOH
PCM-B3LYP	3.27	0.473	6.17	3.30 ^j	Cyclohexane
C522					
B3LYP	3.42 (3.34)	0.370 (0.368)	5.34 (5.39)	3.45 ^p	
PCM-B3LYP	3.14	0.463	6.24	3.05 ^j	EtOH
PCM-B3LYP	3.24	0.475	6.21	3.25 ^j	Cyclohexane

TABLE I. (Continued.)

System/method	$E(S_1)$	Theor. f	μ_{01}	Expt. Energy (μ_{01}) [f]	Solvent
C153					
TDA-BLYP ^k	2.90				
B3LYP	3.31 (3.23)	0.331 (0.333)	5.14 (5.21)	3.37 ^p (5.51) [0.37] ^f	
PCM-B3LYP	3.04	0.422	6.05	2.95 ^j (5.71) [0.373] ^m	EtOH
PCM-B3LYP	3.15	0.434	6.03	3.15 ^j (5.84) [0.408] ^s	Cyclohexane

^a $a_0=10.00$ a.u., $\epsilon=24.55$, $n^2=1.847$.^bReference 14.^cReference 16.^dReference 61.^e $a_0=10.0$ a.u., $\epsilon=78.39$, and $n^2=1.776$.^fReference 18.^g $a_0=11.00$ a.u., $\epsilon=24.55$, and $n^2=1.847$.^hReference 65.ⁱReference 19.^jReference 9.^kReference 31.^lReference 32, excitation energy in *n*-hexane was obtained from an average of 400 snapshots of the molecular dynamics (MD) simulations.^mReference 12.ⁿReference 64.^oReference 69.^pExperimental gas-phase S_0-S_1 , Reference 6.^qReference 60.^rReference 7.^sReference 11.

B3LYP functional. This might be attributed to the tendency to overestimate and underestimate the excitation energy by the SCRF-S model and the B3LYP functional, respectively. Consequently, the *m*CAMB3LYP and CAMBLYP energies that are overestimated in the gas phase are exacerbated in the SCRF-S model. For B3LYP, the SCRF-S excitation energies are larger (by 0.03–0.07 eV) compared to the corresponding PCM (with MAE of 0.03 eV) values. This suggests that excitation energies of *m*CAMB3LYP and CAMBLYP are likely improved with the PCM and the use of diffuse functions, assuming the reduction in excitation energy observed in C120 holds for other coumarins. Thus, using PCM with more flexible basis sets might bring the *m*CAMB3LYP errors closer to those obtained with PBE0 (MAE of 0.11 eV). However, it is unlikely that using PCM with larger basis sets would bring the CAMB3LYP errors to an acceptable range for these systems. Overall, we found that the predicted

B3LYP and PBE0 S_0-S_1 energies in cyclohexane are in excellent agreement with experiment. The errors for *m*CAMB3LYP and CAMB3LYP are slightly larger than those obtained in the gas phase. The trends predicted for the gas phase S_0-S_1 energy to shift to the red with an increasing degree of alkylation for the nonfluorinated (C120 < C1 < C480) and for the trifluorinated series (C151 < C307 < C152 < 152A < C522 < C153) also hold true in cyclohexane, and are confirmed by a collection of experimental values in different studies.

For ethanol, the SCRF-S model and the PCM appear to overestimate S_0-S_1 energies, suggesting the H-bonding effects are significant, especially in C120 and C151. The overall errors for PCM, however, remain low for B3LYP (0.11 eV) and PBE0 (0.21 eV). The MAEs using the SCRF-S model are 0.13, 0.27, and 0.48 eV for the B3LYP,

TABLE II. S_1 TPA cross section (in GM, using FWHM=0.2 eV) and excited state maximum (in parentheses) for C120. Experimental TPA cross section of 19 GM (not a maximum value) measured at 3.29 eV in ethanol, (Ref. 16); experimental TPA cross section of 14 GM (not a maximum value) measured at 4.13 eV in water (Ref. 18).

Method	SRQR		DRQR-SOS (5)	
	δ_G	δ_L	δ_G	δ_L
CAMB3LYP/6-31G*	5.1(4.34)	3.6(4.34)	6.8(4.35)	4.7(4.35)
PBE0/6-31G*	6.4(4.13)	4.4(4.13)	6.9(4.14)	4.7(4.14)
B3LYP/6-31G*	6.6(4.03)	4.6(4.04)	6.9(4.05)	4.8(4.05)
CAMB3LYP/6-311G**	5.2(4.30)	3.7(4.30)	6.5(4.31)	4.4(4.31)
PBE0/6-311G*	6.5(4.10)	4.5(4.10)	6.5(4.12)	4.5(4.11)
B3LYP/6-311G**	6.7(4.01)	4.7(4.01)	6.8(4.02)	4.7(4.01)
CAMB3LYP/6-311++G**	5.5(4.25)	3.9(4.25)	5.9(4.26)	4.0(4.26)
PBE0/6-311++G**	6.9(4.06)	4.8(4.06)	6.8(4.07)	4.7(4.07)
B3LYP/6-311++G**	7.1(3.96)	5.0(3.96)	7.0(3.97)	4.9(3.97)
SCRF-S-B3LYP/6-311++G** ^a	13.9(3.69)	9.5(3.69)	17.4(3.70)	11.7(3.69)
SCRF-S-CAMB3LYP/6-311++G** ^a	13.2(4.00)	9.0(4.00)	15.5(4.01)	10.6(4.01)
SCRF-S-B3LYP/6-311++G** ^b	14.1(3.70)	9.6(3.70)	17.6(3.72)	11.9(3.71)
SCRF-S-CAMB3LYP/6-311++G** ^b	13.8(4.01)	8.9(4.01)	15.3(4.03)	10.5(4.02)

^a $a_0=10.00$ a.u., $\epsilon=78.39$, and $n^2=1.776$ (water).^b $a_0=10$ a.u., $\epsilon=24.55$, and $n^2=1.847$ (EtOH)

TABLE III. Ground and excited state dipole moments (in D) and TPA cross sections for C120 using the two-state approximation.

Method	μ_0	μ_{S1}	μ_{S2}	μ_{S3}	δ_G	Solvent
CAMB3LYP/6-31G*	6.3	8.3	7.5	2.6	4.8	EtOH
PBE0/6-31G*	6.4	9.0	8.3	2.4	7.5	
B3LYP/6-31G*	6.3	9.1	8.4	2.2	8.2	
CAMB3LYP/6-311G*	6.4	8.3	7.4	2.6	5.0	
PBE0/6-311G*	6.4	8.9	8.1	2.3	7.6	
B3LYP/6-311G**	6.4	9.1	8.2	2.2	8.3	
CAMB3LYP/6-311++G**	6.7	8.5	7.4	2.6	4.7	
PBE0/6-311++G**	6.6	9.0	8.3	2.2	7.3	
B3LYP/6-311++G**	6.7	9.2	8.3	2.1	8.0	
Expt. ^c		7.9				
PCM-PBE0/6-31G*	9.4	14.5	12.3	3.7	33.6	Water
PCM-B3LYP/6-31G*	9.4	14.5	12.4	3.7	33.0	
PCM-PBE0/6-311G**	9.6	14.7	12.0	11.7	34.9	
PCM-B3LYP/6-311G**	9.6	14.8	12.2	11.4	34.4	
SCRF-S-CAMB3LYP/6-311++G** ^a	9.5	12.6	10.5	11.4	14.5	
SCRF-S-B3LYP/6-311++G** ^b	9.6	13.4	11.2	10.5	19.1	
PCM-B3LYP/6-311G**	9.8	15.2	12.4	11.7	36.5	
SCRF-S-CAMB3LYP/6-311++G** ^a	9.7	12.8	10.7	11.7	14.6	
PCM-B3LYP/6-311++G**	10.4	15.9	13.0	12.3	42.0	
SCRF-S-B3LYP/6-311++G** ^a	9.8	13.6	11.4	10.8	18.9	

^a $a_0=10.00$ a.u. $\epsilon=78.39$, and $n^2=1.776$ (water).^b $a_0=10.00$ a.u. $\epsilon=24.55$, and $n^2=1.847$ (EtOH).^cEstimated from the Lippert-Mataga relationship using μ_g value of 6.0 D and r value of 3.41 Å (Ref. 14).

*m*CAMB3LYP, and CAMBLYP, respectively. The latter two functionals overestimate all the S_0 - S_1 excitation energies, with C120 having the largest error. In fact, the continuum solvation models fail to predict the observed blueshift in the excitation energy in water with respect to EtOH (see Table I). This might be attributed to the H bonding, which is not accounted for in the continuum models of solvation. In C120 (and C151), water and alcoholic solvents can form hydrogen bonds with the nitrogen (A) or oxygen (B) at the amine and the carbonyl groups, respectively, and/or accepting a H bond at the amine hydrogens (C).⁵⁶⁻⁵⁸ The B and C interactions strongly stabilize the positive and negative charges on the amino nitrogen and carbonyl oxygen, respectively, in ICT excited state of C120, leading to a redshift in the ICT excitation energy in the more acidic water compared to alcohols. The A and B interactions are present in all 7-aminocoumarins, while the C interactions are unique to the nonalkylated and the *N*-alkylated (not *N*-dialkylated) systems. However, the blueshift in the S_0 - S_1 excitation energy in water with respect to alcohols has been attributed to the A interaction that better stabilizes the ground state than the ICT excited state.^{57,58} Interestingly, previous DFT studies of C151 with one water molecule did not locate a stable A-type conformer in the ground state. Therefore, calculations of C120 in water and methanol clusters embedded in a dielectric continuum are important to shed more light on the effects of H bonding on the solution spectra. Thus, we have carried out PCM-TDDFT calculations on C120 with a small number of water and methanol molecules. Although some conformers with the A and C interactions possess blueshifts in excitation energies, the computed Boltzmann averaged excitation

energies (neglecting entropy) are similar for water and methanol [see Table 2S in the EPAPS (Ref. 68) Supporting Information Section]. The inclusions of entropy, which requires more sophisticated treatments for low frequency modes beyond the so called rigid rotor and harmonic oscillator approximation, are under consideration. Calculations for larger clusters using Monte Carlo optimization⁵⁹ are also being carried out and will be reported in the future.

We now consider the OPA intensity, which can be measured with the μ_{ge} or f values that are available for C152 (Ref. 60) and C153 (Ref. 11) in a number of solvents. For C153, the emission and absorption transition moments were reported to be the same to within the experimental uncertainty.¹¹ For other systems, the μ_{ge} and f values in solutions were obtained by using published maxima of absorption coefficients and corresponding full width at half maxima (FWHM), and by integrating the appropriate spectral bands, which were approximated by Gaussians. Although gas-phase absorption spectra for a number of coumarins have been reported, the corresponding absolute intensities were not measured, except for the f value of 0.37 for C153,⁷ which is within the range (0.33–0.44) of the computed values. For other systems, our comparison between theory and experiment is largely limited to values obtained in alcoholic solutions. Experimental f values in cyclohexane and water are also reported for some systems.

The value of f for C120 in water (0.325) was obtained by digitization of the OPA spectrum reported by Overway and Lytle.¹⁸ The corresponding value in ethanol (0.318) was obtained from the spectral data reported by Fisher *et al.*¹⁶ and Reynolds and Drexhage.⁶¹ These experimental oscillator

TABLE IV. Computed maximum TPA cross section (in GM, using FWHM=0.2 eV) and corresponding transition energy (in parentheses) compared with the experiment. Single “*” denotes “not a maximum value.”

System/method	SQR		Expt.	
	δ_G	δ_L	δ	δ_G (TS) ^a
C120				
B3LYP/6-311++G**	7.1 (3.96)	5.0 (3.96)		
SCRF-S-mCAMB3LYP/6-311++G** ^b	13.7 (3.82)	9.3 (3.82)		
SCRF-S-CAMB3LYP/6-311++G** ^b	13.2 (4.00)	9.0 (4.00)		
SCRF-S-B3LYP/6-311++G** ^b	14.1 (3.70)	9.6 (3.70)	14 (4.13) ^{c,*}	4 ^{a,d}
SCRF-S-CAMB3LYP/6-311++G** ^c	13.8 (4.01)	8.9 (4.01)		
SCRF-S-mCAMB3LYP/6-311++G** ^c	13.8 (3.84)	9.4 (3.84)		
SCRF-S-B3LYP/6-311++G** ^c	13.9 (3.69)	9.5 (3.69)	19 (3.29) ^{f,*}	
C1				
B3LYP/6-311G**	18.6 (3.73)	12.7 (3.73)		
SCRF-S-CAMB3LYP/6-311G** ^g	26.2 (3.91)	17.8 (3.91)		
SCRF-S-mCAMB3LYP/6-311G** ^g	28.0 (3.70)	19.2 (3.70)		
SCRF-S-B3LYP/6-311G** ^g	28.6 (3.53)	19.6 (3.53)	104 (3.29) ^{f,*}	8 ^{a,h}
C480 (C102)				
B3LYP/6-311G** (syn)	14.9 (3.61)	10.2 (3.61)		
SCRF-S-CAMB3LYP/6-311G** (syn) ⁱ	21.7 (3.79)	14.9 (3.79)		
SCRF-S-mCAMB3LYP/6-311G** (syn) ⁱ	22.1 (3.58)	15.2 (3.58)		
SCRF-S-B3LYP/6-311G** (syn) ⁱ	21.7 (3.42)	14.8 (3.42)	160 (3.17) ^j	9 ^{a,k}
C151				
B3LYP/6-311G**	10.3 (3.74)	7.1 (3.74)		
SCRF-S-B3LYP/6-311G** ^g	14.0 (3.45)	9.5 (3.45)	47 (3.28) ^{f,*}	14 ^{a,l}
SCRF-S-mCAMB3LYP/6-311G** ^g	15.4 (3.60)	10.5 (3.60)		
SCRF-S-CAMB3LYP/6-311G** ^g	16.8 (3.79)	11.5 (3.79)		
C307				
B3LYP/6-311G**	15.4 (3.56)	10.5 (3.56)		
SCRF-S-CAMB3LYP/6-311G** ⁱ	29.0 (3.55)	19.8 (3.55)		
SCRF-S-mCAMB3LYP/6-311G** ⁱ	27.1 (3.34)	18.5 (3.34)		
SCRF-S-B3LYP/6-311G** ⁱ	25.1 (3.17)	17.1 (3.17)	19 η (3.20) ^m	

^aTPA cross sections are obtained with experimental μ_{ge} in Table I, $\Delta\mu_{ge}$ from time-resolved microwave dielectric absorption measurements in benzene (Ref. 62), computed angles (C120=160°, C1=165°, C480=164°, and C151=164°) between μ_{ge} and $\Delta\mu_{ge}$, and Gaussian line shapes (FWHM=0.2 eV) using the two-state approximation.

^b $a_0=10$ a.u., $\epsilon=78.39$, and $n^2=1.776$ (water).

^cExperimental TPA cross section measured in water (Ref. 18).

^d $\Delta\mu_{ge}=2.4$ D, using $\Delta\mu_{ge}=4.1$ – 6.2 D (electro-optic) (Ref. 62) gives $\delta_G(\text{TS})=11$ – 26 GM; and using $\Delta\mu_{ge}=1.90$ D (Ref. 14) (solvatochromism) gives $\delta_G(\text{TS})=2$ GM; and using $\Delta\mu_{ge}=3.97$ D (Ref. 66) (solvatochromism) gives $\delta_G(\text{TS})=11$ GM.

^e $a_0=10$ a.u., $\epsilon=24.55$, and $n^2=1.847$ (EtOH).

^fExperimental TPA cross section measured in EtOH (relative error of about 1/2 of magnitude) (Ref. 16).

^g $a_0=11$ a.u., $\epsilon=24.55$, and $n^2=1.847$ (EtOH).

^h $\Delta\mu_{ge}=2.9$ D, using $\Delta\mu_{ge}=7.3$ – 7.8 D (Ref. 62) (electro-optic) gives $\delta_G(\text{TS})=50$ – 57 GM; and using $\Delta\mu_{ge}=2.72$ D (Ref. 15) (solvatochromism) gives $\delta_G(\text{TS})=7$ GM.

ⁱ $a_0=11$ a.u., $\epsilon=32.63$, and $n^2=1.758$ (MeOH).

^jExperimental TPA maximum cross section measured in MeOH (Ref. 19).

^k $\Delta\mu_{ge}=3.0$ D, using $\Delta\mu_{ge}=2.11$ D (Ref. 67) (solvatochromism) gives $\delta_G(\text{TS})=4$ GM.

^l $\Delta\mu_{ge}=4.4$ D, using $\Delta\mu_{ge}=1.7$ D (Ref. 67) (solvatochromism) gives $\delta_G(\text{TS})=2$ GM; using $\Delta\mu_{ge}=2.81$ D (Ref. 64) (solvatochromism) gives $\delta_G(\text{TS})=6$ GM; and using $\Delta\mu_{ge}=4.35$ – 7.01 D (Ref. 5) (electro-optic) gives $\delta_G(\text{TS})=14$ – 35 GM.

^mExperimental TPA maximum cross section measured in MeOH; η is the quantum yield (Ref. 17). $\eta=0.61$ (Ref. 58), 0.56 (Ref. 61) in EtOH. $\eta=0.90$ in 50% EtOH (Ref. 9).

strengths are slightly smaller than the computed values of about 0.4–0.5, with those predicted by CAMB3LYP and *m*CAMB3LYP functionals being the larger ones. The transition dipoles and oscillator strengths obtained with the PCM are also slightly larger than the corresponding SCRF-S values. The overall errors for PCM, however, remain low for

B3LYP (0.41 D) and PBE0 (0.55 D). The MAEs using the SCRF-S model are 0.28, 0.48, and 0.71 D for the B3LYP, *m*CAMB3LYP, and CAMBLYP, respectively. It is encouraging that the predicted *m*CAMB3LYP transition dipoles are in accordance with those of B3LYP and PBE0. The predicted changes in μ_{ge} from cyclohexane to MeOH/EtOH are small.

This is consistent with the lack of dependence on solvents for absorption transition moments of C102 and C153, as observed by Lewis and Maroncelli.¹¹

Upon alkylation, the computed μ_{ge} and f values of the ICT band show a slight increase, as predicted by the PCM using the PBE0 (0.07 and 0.61 D) and B3LYP (0.07 and 0.64 D) functionals for C1 [see an expanded version of Table I in the EPAPS (Ref. 68) Supporting Information Section]. This is in good agreement with the experimental shifts of 0.08 and 0.74 D for the oscillator strength and transition moment, respectively. Note that these observed shifts are also well reproduced using the SCRF-S model with the B3LYP (0.08 and 0.68 D) and the *m*CAMB3LYP (0.10 and 0.74 D) functionals but not as accurate with the CAMB3LYP (0.12 and 0.79 D) functional. The alkylation of C120 to create C480 produces a similar increase (0.09 and 0.95 D) in the experimental f and μ_{ge} values from the absorption data of Fisher *et al.*^{16,19} and of Reynolds and Drexhage.⁶¹ However, the corresponding computed values for the *syn* and *anti* conformations of C480 show smaller increases from that of C120, which is overestimated by the continuum solvation models. Furthermore, the two isoenergetic *syn* conformations are 0.5 and 0.2 kcal/mol lower in energy than their *anti* counterparts in the gas phase and in MeOH, respectively. Thus, rapid *syn-anti* conversions may occur at room temperature, leading to a different mixture of conformers and corresponding intensities for the ICT band. Similarly, the *syn* conformers of the trifluorine substituted C153 are 0.3 kcal/mol lower in energy than their *anti* counterparts in the gas phase. This is identical to the *syn-anti* relative energy reported by Cave and Castner.²⁹ However, recent calculations by Sulpizi *et al.*^{30,31} for C153 using the nonhybrid BLYP functional with a plane-wave basis set and pseudopotentials revealed that the *anti* conformer has the lowest energy. The other *anti* conformer was located at 0.8 kcal/mol above the lowest *anti* congener. The two *syn* conformers were found to be 0.8 and 1.1 kcal/mol above the lowest *anti* structure. We found that the *syn* and *anti* conformers of C153 are isoenergetic in EtOH.

The shifts in transition moment for the trifluorine derivatives follow the alkylation trends discussed above, increasing from C157(4.97 D) < C307(5.52 D), C152(5.31 D) < C152A(5.88 D), and C153(5.71 D). The predicted transition moments (5.23–5.69 D) for C151 are significantly larger than experimental value (4.97 D) in EtOH due to the importance of H bonding. For C153, the predicted transition values vary from 5.84 D (B3LYP) to 6.40 D (CAMB3LYP). The corresponding experimental value of 5.71 D was obtained by using the peak extinction coefficient reported by Reynolds and Drexhage⁶¹ and the FWHM reported by Gustavsson *et al.*¹² This value is in good agreement with the transition dipole moments of 5.03–5.71 D reported by Lewis and Maroncelli¹¹ for C153 in methanol, as obtained by numerically integrating the spectrum and scaling them with different refractive index correction factors. Their nonscaled value of 5.80 D for the emissive transition dipole moment, which was reported to be the same as the absorptive moment, is slightly (0.1 D) larger than the value integrated with Gaussian line shape above. The predicted errors of

0.3–0.4 D for B3LYP and *m*CAMB3LYP are close to the estimated experimental uncertainty of 0.3 D (5%) for C153.¹¹

B. Two-photon absorption

The TPA absorption cross sections are listed in Tables II–IV for various basis sets and functionals along with available cross sections. In addition, cross sections obtained with experimental μ_{ge} (in Table I) and the difference between the ground and first excited state dipole moments ($\Delta\mu_{ge}$) using the two-state approximation are also listed for four coumarins. These experimental $\Delta\mu_{ge}$ have been estimated by several experimental methods, including time-resolved microwave dielectric absorption measurements,⁶² which are claimed to be superior. Note that these experimental studies were not carried in the same solvents as in the TPA studies. Thus, the cross sections obtained from these quantities offer qualitative rather than quantitative comparisons with the TPA measurements. The consensus in OPA intensity line shape at room (or higher) temperature appears to be Gaussian. However, both Gaussian and Lorentzian functions are often used to compute TPA cross sections. The difference between the maxima of the two line shape functions, as shown for C120 in Table II, is a factor of 1.48, with the Gaussian cross (δ_G) section being larger than the corresponding Lorentzian (δ_L) value. TPA cross sections computed with the single residue of the quadratic response function are denoted by SRQR. DRQR-SOS refers to values computed with the SOS method using the DFT ground state dipoles, transition dipoles and excitation energies from linear response TDDFT, and the excited dipoles and excited-to-excited transition dipoles from the double residue quadratic response function. The latter approach is computationally more demanding, but offers insights into the mechanism of TPA. For C120 with the lowest five excited states in the SOS expression, the two methods yield cross sections at the TPA resonance within a few GM of each other (see Table II). Our SOS calculations reveal a type-II TPA for the first state of C120, in which the TPA is driven by $\Delta\mu_{ge}$. Thus, the difference in the cross sections obtained from the two-state and the five-state approximation is (1–3 GM) small (cf. Tables II and III). We found that the cross sections are not significantly affected by the basis set. For C120, changes of δ_G upon going from the 6-31G(*d*) to the 6-311+G(*d,p*) basis set using the SRQR method are less than 1 GM for all functionals. For the largest basis set, variations in the peak cross sections are within 2 GM, as obtained with CAMB3LYP (5.5 GM), PBE0 (6.9 GM), and B3LYP (7.1 GM) functionals. Small variations among the functionals are also observed in solvents for C120 and other systems.

In solvents, the predicted cross sections of 13–14 GM for C120 (Table IV) are significantly larger than those in the gas phase, due to the increase in $\Delta\mu_{ge}$ (Table III). The cross sections predicted by the PCM are significantly larger than those obtained with the SCRF-S using the two-state approximation. This can be attributed to larger excited state dipole moments predicted by the PCM. It is not straightforward to compare these computed values with experiment, since the TPA cross sections of 19 and 14 GM measured at 3.29 and

4.13 eV in ethanol¹⁶ and water,¹⁸ respectively, are not the local maxima of the TPA spectra. The maxima are likely located at higher (lower) energy with even larger cross sections than the predicted values for ethanol (water). Interestingly, these cross sections fall in the range (2–26 GM) of values obtained for the two-state approximation using experimental μ_{ge} and $\Delta\mu_{ge}$.

The predicted TPA cross section (energy) increases (decreases) with an increasing degree of alkylation. This is consistent with increase in $\Delta\mu_{ge}$ and μ_{ge} upon alkylation that has been predicted²⁹ and experimentally observed.⁶² However, the increase in the cross section upon an increasing degree of alkylation (C120 < C1 < C480) is not quantitatively reproduced. The experimental cross sections of 104 and 160 GM for C1 and C480 (Table IV) are significantly larger than the corresponding predicted values of 28 (C1) and 22 (C480) GM. These discrepancies can be attributed to the uncertainty both in the predicted and observed cross sections. In addition to the errors from the linewidth functions as discussed above, the computed errors might be attributed to the specific solvent interactions that are not accounted for in the SCRF model. Experimentally, the errors for TPA cross sections for C1 and C120 have been reported of about half order of magnitude.¹⁶ For C480 (C102), the TPA cross section was obtained by relative fluorescence measurement¹⁹ assuming unity fluorescence quantum yield for both the *p*-bis-*o*-methyl-styrylbenzene (BMSB) reference and C480, which was reported to be 0.58 (Ref. 61)–0.95 (Ref. 9) in EtOH. Very high (0.995–0.870) quantum yields were reported for BMSB in a few nonpolar solvents, but was not given for EtOH.⁶³ Thus, an adjustment the TPA cross section of C480 based on measured quantum yields would be useful.

For the trifluorinated series, the predicted TPA cross sections follow the alkylation trends previously observed. The TPA maximum (δ_G) cross section (energy) is predicted (SCRF-*S*-B3LYP/6-311G**) to increase (decrease) from 14.0 GM (3.45 eV) to 25.1 GM (3.17 eV) for C151 and C307, respectively. The TPA spectrum of C151 in EtOH taken from 2.95 to 3.28 eV shows a cross section of 47 GM at 3.28 eV,¹⁶ which is comparable to the OPA maximum of 3.24 eV in the same solvent. The experimental TPA cross section of 47 GM for C151 is more than twice maximum cross section of $19\eta \pm 5.5$ GM obtained in MeOH at 3.20 eV for C307,¹⁷ even with the fluorescence quantum yield $\eta = 1$. Thus, the observed redshift in the TPA maximum of C151 upon alkylation is consistent with the theoretical prediction. However, the decrease in the corresponding cross section is in discordance with theory. It should be noted that the experimental cross section of 47 GM reported for C151 has a much larger uncertainty (half order of magnitude)¹⁶ than that of C307. Thus, new experimental studies on the TPA cross sections of C151 and other coumarins would be useful in verifying the predicted results.

IV. SUMMARY AND CONCLUSIONS

We found that gas-phase excitation energies for C152, C152A, C522, and C153 are well reproduced with the 6-311G(*d,p*) basis set, with the mean absolute errors of 0.03,

0.08, 0.10, and 0.32 eV, for PBE0, B3LYP, *m*CAMB3LYP ($\alpha = 0.19$ and $\beta = 0.19$), and CAMB3LYP ($\alpha = 0.19$ and $\beta = 0.46$), respectively. The corresponding sets of 0.16, 0.05, 0.06, and 0.29 eV are found for the 6-311+ + G(*d,p*), which has negligible differences in S_0 - S_1 excitation energies and oscillator strengths from the larger aug-cc-pVTZ basis set. All the four functionals predict S_0 - S_1 energy to shift to the red with an increasing degree of alkylation. Trifluorination at the 4-methyl group gives pronounced redshifts that increase in magnitude with a higher degree of alkylation. These predictions are found to be in agreement with the experiment.

The 6-311G(*d,p*) excitation energies predicted by the SCRF-*S* model overestimate experimental S_0 - S_1 energies by 0.05, 0.22, and 0.42 eV for the B3LYP, *m*CAMB3LYP, and CAMBLYP, respectively, in cyclohexane. In MeOH/EtOH, the MAEs for excitation energy (transition moment) are 0.13 (0.28), 0.27 (0.48), and 0.48 (0.71) eV (D) (D) for the B3LYP, *m*CAMB3LYP, and CAMBLYP, respectively. The corresponding MAEs for the PCM are 0.11 (0.41) and 0.21(0.55) eV (D) for B3LYP and PBE0, respectively. The larger errors of excitation energy predicted in alcoholic solvents are attributed to the H bonding, which is not accounted for in the continuum solvation models.

The first excited state of coumarins has large TPA cross sections, which are driven by the change in dipole moments between the ground and the more polar first excited state. We observed a large enhancement in the TPA cross section in polar solvents due to the increase in excited state dipole moments compared to the corresponding ground state values. We found that the variations in the TPA peak cross sections are small (1–3 GM) among the various basis sets and functionals, including the *m*CAMB3LYP functional which significantly reduces the errors in the TPA and OPA resonances. The predicted cross sections are largely consistent with experiment to within the experimental uncertainties. Some large deviations may be attributed to the large uncertainties in the experimental cross sections. Thus, new experimental TPA studies for these coumarins would be useful in verifying the predicted results.

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